Solid State Communications, Vol. 85, No. 11, pp. 921-924, 1993. (3/93)
Printed in Great Britain.

0038-1098/93$6.00+.00
Pergamon Press Ltd

NEEDLE-LIKE CRYSTALLIZATION OF Ni DOPED AMORPHOUS SILICON THIN FILMS

T. Hempel and O. Schoenfeld
Institut für Experimentelle Physik, Technische Universität Magdeburg, O-3010 Magdeburg, FRG

F. Syrowatka
Fachbereich Physik, Martin-Luther-Universität Halle-Wittenberg, O-4020 Halle, FRG

(*Received* 15 *January* 1993 *by T. Martin*)

The crystallization behaviour of Ni doped co-sputtered amorphous silicon thin films (MSP a-Si(Ni)) is investigated by means of NIR-VIS-UV transmission spectroscopy and STEM. Using the change in optical transmission spectra of crystallized a-Si(Ni) thin films the crystallization kinetics is described. During a thermal annealing process the crystalline phase forms at one edge of the sample and then extends across the whole thin film. At the crystallization frontier a needle morphology of single crystals is observed with STEM which may result from solid state diffusion of nickel through the amorphous matrix. Using a long term thermal treatment we achieve the formation of extensive monocrystalline networks.

1. Introduction

Metal silicides in thin films have a wide range of applications in electronics[1,2]. For most of these applications, silicides are formed by interfacial reactions between metal films and silicon[1,2]. Metal ion implantation has been employed to produce buried metal silicide layers in single crystal silicon[3]. Cammarata et al.[4] have reported the use of ion implantation to produce buried nickel silicide precipitations in amorphous silicon thin films. Unlike the case for interfacial reactions between nickel and silicon,[1,2] where the first of several possible intermetallic phases to form is the most nickel-rich phase, Ni_2Si, the first (and only) phase to form in those nickel ion implanted films is the most silicon-rich phase, $NiSi_2$. It has been suggested that this difference in first phase formation behaviour is due to the effect of interfacial energies on the nucleation kinetics[4]. Furthermore an enhancement in the kinetics of crystallization of the CVD - a-Si (Ni) was also reported, apparently owing to the migration of nickel silicide precipitations[4]. While Cammarata et al.[4] investigated the nucleation and growth kinetics of $NiSi_2$ precipitation in nickel implanted amorphous silicon thin films we have studied the crystallization process in dc magnetron co-sputtered a-Si (Ni) thin films (MSP - a-Si(Ni)). Using a specific thermal annealing treatment the growth of "needle-like" monocrystalline networks is realized.

2. Experimental Procedure

Amorphous silicon thin films with a thickness of 50 nm, 200 nm and 650 nm containing nickel impurities were deposited with MSP - a-Si (Ni)) onto quartz glass and Corning 7059 held at 150°C. Nickel impurities were built into the amorphous silicon thin films with a concentration of about 0.5 at% measured in an area of 1 μm^2 by means of STEM x-ray microanalysis. During the deposition the dc power was held at 170 W with a target voltage of 420 V; the pressure of the argon gas was held at 0.37 Pa. A lightly boron doped silicon target was used where the distance between target and substrate was 100 mm. The thermal annealing procedure took place in a quartz tube furnace flushed with argon. The temperature was measured by a Fe-constantan thermocouple which was attached directly to the back of the sample. The range of temperature used in the present study was bounded by two experimental factors. Firstly when samples were annealed at temperatures of 650°C and above the entire crystallization reaction was completed within 15 minutes (the shortest time that could be accurately used in this work), thereby preventing the determination of amorphous to crystalline transition at these temperatures. Secondly when samples were annealed at temperatures of 450°C and below no crystallization was observed at annealing times up to 36 h (the longest time that was used in this work).
At a given annealing temperature the attached annealing times were determined using changes in optical transmission data due to amorphous to crystalline phase transition as reported by Blum and Feldmann[5]. We have used a NIR-VIS-UV spectrometer Shimadzu UV 3014 at wavelengths from 300 nm to 2600 nm. At 2.6 eV (480 nm) for example crystallized a-Si(Ni) thin films with a thickness of 650 nm exhibit an absorption coefficient α of about $5.6\ 10^4\ cm^{-1}$, while as-deposited amorphous thin films exhibit an α at least three orders of magnitude higher. The visible brightening of the thermally annealed a-Si(Ni) thin films accompanies the amorphous to crystalline transition as confirmed by STEM investigations. Thus the transmission of these thin films at 2.6 eV is a sensitive indication of the degree

of crystallization.

The structural properties were investigated by means of a STEM VG HB 501 UX at an accelerating voltage of 100 kV. Plan view electron micrographs at an electron optical magnification up to 10^6 times, were recorded for subsequent determination of crystal growth characteristics of 200 nm and 50 nm thin films. To permit structural and compositional analysis, microanalysis on the STEM was carried out at 50 nm thin films under analytical conditions using a 1 nm^2 electron probe and an energy dispersive x-ray microanalysis system from KEVEX. Specimens were prepared for electron microscopy by means of HF etching to remove the thin films from the glass substrate. The freestanding films were floated onto electron microscope grids.

3. Experimental Results

The investigation of crystallization kinetics was followed by observing optical transmission data of the amorphous thin films as they were heated at various temperatures. In practice the changes of these spectra started at one side of the thin film and expanded across the whole sample. Due to this fact we can observe the migration of the crystallization frontier during the thermal annealing process. Thus we were able to detect the velocity of the crystallization at a given temperature on the same sample. Figure 1 describes the temperature dependence of the growth rates of the crystallized MSP a-Si(Ni) thin films which have a thickness of 200 nm. The slope of the Arrhenius plot determines the dependence of thin film's ability to crystallize in this special manner.

Figure 2 shows a low magnification plan view transmission electron micrograph of a 200 nm thin film which was annealed at 560°C for 2h. The figure shows the microscopical structure at the crystallization frontier of a half-crystallized MSP a-Si(Ni) thin film. In addition to the nickel-rich precipitations (which appear as "black dots"), some of the amorphous silicon had crystallized at the

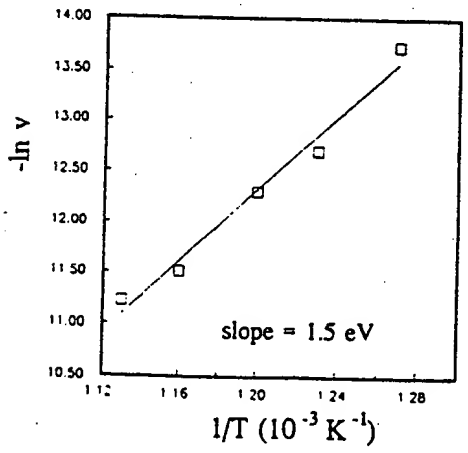

Fig.1: Growth rate v or velocity of the crystallization frontier in μm/s versus the inverse annealing temperature of 200 nm MSP-a-Si(Ni) thin films.

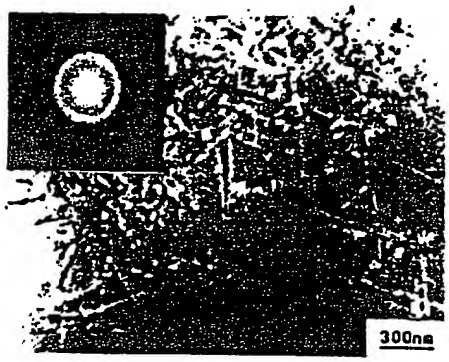

Fig.2: Low magnification plan view micrograph of the crystallization frontier of an MSP-a-Si(Ni) thin film annealed at 560°C for 2h.

phase transition. Selected area diffraction revealed that each transformed region was a single crystal.

A typical area of crystallized silicon is shown in Figure 3. As can be seen amorphous silicon is transformed to silicon with a needle morphology. In each crystallized region the growth of most of the needles takes place at angles of 71° to each other. This angle indicates that the needles grow in [111] directions. An 8h anneal at 560°C of a sample without nickel impurities produced no detectable crystallization and no optical thin film brightening. In order to observe approximately the same amount of crystallization in an undoped sample, an 2h anneal at about 750°C was necessary resulting in polycrystalline regions possessing equiaxed grains.

As shown in Figure 4 x-ray microanalysis revealed a nickel-rich region at the leading edge of each needle. This suggests, that the needle-like crystallization may be "catalyzed" by solid state diffusion through migrating nickel, dissolving amorphous silicon at one edge and rejecting crystallized silicon at the opposite edge, as also discussed by Nygren et al.[6] for Indium doped a-Si thin films.

Diffraction patterns of needles and its edges indicated no detectable difference. We have to assume that both phases have almost the same crystal structure and atomic con-

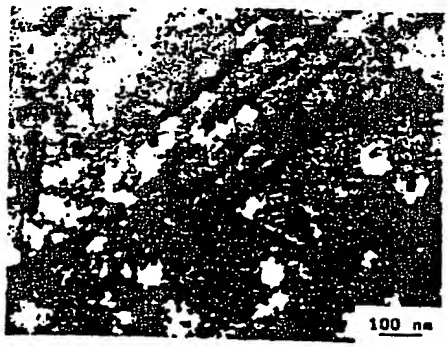

Fig.3: High magnification electron micrograph showing single crystal silicon formed at 560°C for 2h.

Ni

Fig.4a: High magnific picture showing a Ni-r two neighboured needl

Fig.4b: X-ray analysis the leading edges o (see Fig. 4a)

stant a_0. From the diffr structure for the c-Si n $NiSi_2$ is the only fcc nicl (a_0=5.39Å), that is almc crystalline Si needles, v edges consist of $NiSi_2$. T microanalysis measurem the a-Si matrix below ar

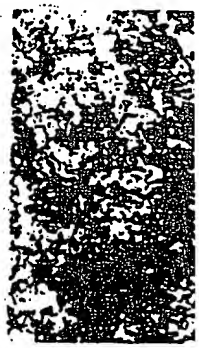

Fig.5: Low magnificat crystallized MSP-a-Si(N 2h.

micrograph of the
-a-Si(Ni) thin film

action revealed that
crystal.
is shown in Figure 3.
transformed to silicon
rystallized region the
place at angles of 71°
at the needles grow in
560°C of a sample
no detectable crystal-
ightening. In order to
ount of crystallization
al at about 750°C was
ne regions possessing

croanalysis revealed a
ge of each needle. This
rystallization may be
ion through migrating
icon at one edge and
opposite edge, as also
Indium doped a-Si thin

d its edges indicated no
assume that both phases
ucture and atomic con-

ctron micrograph showing
560 C for 2h

Fig.4a: High magnification electron micrography analysis picture showing a Ni-rich region at the leading edges of two neighboured needles

Fig.4b: X-ray analysis picture showing a Ni-rich region at the leading edges of the two neighboured needles (see Fig. 4a)

stant a_0. From the diffraction patterns follows a diamond structure for the c-Si needles with an a_0 of 5.43 Å. Since $NiSi_2$ is the only fcc nickel silicide with an atomic constant (a_0=5.39Å), that is almost the same one as for the monocrystalline Si needles, we have to assume, that the needle edges consist of $NiSi_2$. This fact is supported by our x-ray microanalysis measurements in which we have to consider the a-Si matrix below and above the needles. Furthermore

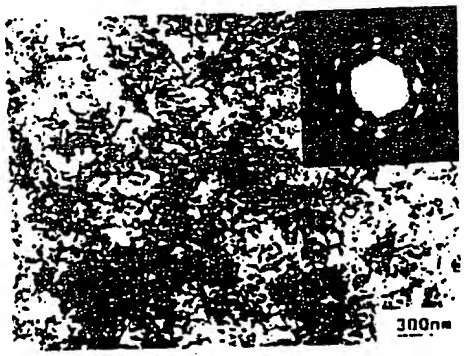

Fig.5: Low magnification plan view micrograph of crystallized MSP-a-Si(Ni) thin films annealed at 560°C for 2h

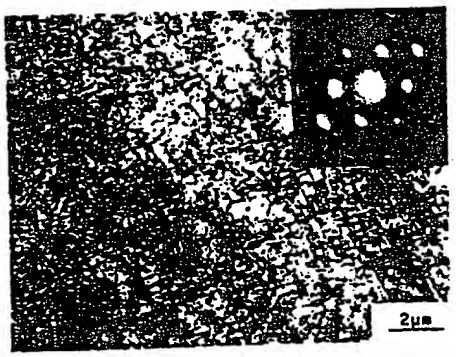

Fig.6: Low magnification plan view micrograph of crystallized MSP-a-Si(Ni) thin films annealed at 560°C for 8h.

we were able to find a transition from the [111] crystal growth direction to the [110] direction at the edges of a few needles. The angel between the two growth directions is 54°. The size of needles with [110] growth is very short and these needles have a silicide precipitate at their leading edges, too. It seems that this crystal growth is caused by a specific cooling process after thermal treatment.

A low magnification plan view electron micrograph of the crystallized phase, behind the crystallization frontier, is shown in Figure 5. This sample is, as are the previous ones, from the same a-Si(Ni) thin film annealed at 560°C for 2h. The figure shows an accumulation of monocrystalline needles in a fine polycrystalline matrix. By means of long term annealing at 560°C for 8h we were able to create a silicon monocrystalline regular network as shown in Figure 6. The associated diffraction pattern shows that the share of the diffraction intensity of the fine crystalline silicon is almost suppressed by the diffraction intensity of the monocrystalline network. The needles have a length of up to a few micrometres and a thickness of about 20 nm. It is not yet clear why such a regular growth took place during the long term annealing process. The crystal growth process had started from several needle accumulations in the amorphous matrix and ended in an expanded monocrystalline network. We assume that the first grown needle initiated a second parallel growth process in a certain distance from the first ones, and that similar processes took place repeatedly.

4 Conclusions

We have investigated the needle-like crystallization in MSP - a-Si(Ni) thin films. Since the crystallization process started at one edge of the sample, we were able to study all phases of the amorphous to crystalline transition at the same thin film. Using a long term thermal annealing treatment we were able to create monocrystalline networks.

References

1. K.N.Tu, in Advances in Electronic Materials, edited by Wessels and G.V.Chin, American Society of Metals, Metals Park, OH, 147 (1986)
2. S.P. Murarka, Silicides for VLSI Applicati ns, Academic Press, Orlando, FL, (1983)
3. A.E.White, - K.T.Sh rt, R.C.Dynes, J.P.Garno, J.M.Gibson, Appl. Phys. Lett. 50, 95 (1987)
4. R.C.Cammarata, C.V.Thompson, C.Hayzelden, K.N.Tu, J. Mater. Res., 10, 2133 (1990)
5. N.A.Blum, C.Feldmann, J. Non-Cryst. Solids 11, 242 (1972)
6. E.Nygren, J.C.McCallum, R.Thornton, J.S.Williams, G.L.Olson, Mat. Res. Soc. Symp. Proc. Vol. 100, Materials Research Society, (1988)

Solid Sta
Printed i

FIELD EN

Centre d'E
1 Lab. vo
B-3001, Be
USSR.
2 Lab Léo

By decreasir
$YBa_2Cu_3O_{6+x}$
diagram was
superconductir
suppressed and
place yielding a
In 123 compo
transition from t
critical currents
critical fields ar
doped $YBa_2Cu_3($
0.50 have much
conducting t
dimensionality
in the heavily d
the other hand
occurs at about

$x=x_c=0.41\pm0.02$ a
range antiferroi
antiferromagneti
we may expect
betw en the sup
transitions, like
fermion supe
communication
measurements of
out on wea
superconductors,
transition.

The $YBa_2Cu_3O_6$
a twinned crystal
grain growth te
treatment was p